

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Articles Treated so as to have Microbicidal Properties

I, STANLEY DUNLOP, a British Subject, of the firm H. D. Fitzpatrick & Co., 3, Gray's Inn Square, London, W.C.1, England, do hereby declare the invention (as communicated to me by Permachem Corporation, a Corporation organised under the laws of the State of Delaware, United States of America, of 5610, Georgia Avenue, West Palm Beach, Florida, United States of America), for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to treated articles characterized by a high degree of toxicity to bacteria and fungi with which they come into contact and to a process for preparing such treated articles. The products are characterized by a low degree of toxicity to the higher animals and by the freedom from discoloration of tissues and other objects with which they come in contact.

The treatment of articles, such as those made of fabrics, rubber goods, paper, leather, felt, synthetic organic plastics, ceramics and other substances, to render them lethal over long periods of storage and use to microorganisms coming into contact with them has long presented a problem for which no ready solution free of other undesirable effects has heretofore been found. The problem of controlling the undesirable effects caused by the invasion of bacteria, viruses and fungi of many kinds in the vegetable and animal kingdoms and the difficulties often encountered in killing the invading populations, not only on living plants and animals but also on the many non-living articles which may serve as carriers and harbors for them, are well known. The advantages of articles which would be effective in killing microorganisms falling on them are apparent as are also the advantages of a method useful in preparing such articles.

Many substances are known which are toxic to bacteria or to fungi, or to both, and many attempts have been made to utilize such substances either alone or combined with other

substances to control undesirable microorganisms. Most substances which have heretofore been available have, however, possessed other undesirable properties which render them unsuited for many uses or which render their application difficult. For widespread use such substances should be non-toxic to humans and the higher animals, they should be non-irritating and non-staining when in contact with sensitive living or inanimate tissues and, for most applications, they should be devoid of odor and color and should not themselves become colored or develop an odor with the passage of time.

It has long been known that silver salts which furnish at least a minimum concentration of silver ions in aqueous mixtures have strong germicidal properties. Such silver compounds have, however, been utilized to only a very limited extent as germicides because of their known effects in staining tissues and in becoming colored when exposed to light, especially when in contact with proteins. Silver compounds which are highly soluble in water, such as silver nitrate, are unsatisfactory for most such uses because they are removed easily by washing and because of their well known effect in coagulating and precipitating protein. Colloidal silver has, of course, been used for certain limited germicidal purposes but is highly undesirable in applications where the development of color or staining cannot be tolerated.

According to the present invention there is provided an article having on the surface thereof a coating comprising a co-precipitated mixture of a sparingly water-soluble silver salt and at least one other sparingly water-soluble compound of another metal of such a nature that it functions as an effective stabilizer of the silver salt against the effect of light normally tending to discolor the silver salt.

Many inanimate substances can be treated to form the coating on their surfaces and produce articles which are lethal to microorganisms falling on their surfaces and which retain this property after long periods of use

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and even after being cleaned repeatedly. Cloth treated by the process so that the fibers become coated or impregnated with the composition is lethal to bacteria and fungi falling on its surface and remains this way after repeated and severe laundering with hot soap solution.

When a high degree of fungicidal effectiveness is also desired, a sparingly water-soluble fungicidal compound of a fungicidal organic acid is also included in the coating the fungicidal salt being selected so that in contact with water it furnishes a fungicidal concentration of the organic acid anions but so that it does not reduce the concentration of silver cations in the aqueous mixture below that necessary to exert the bactericidal effect of the silver cations. In many instances the mixture of silver salt, the light stabilizer for the silver salt, and the fungicidal salt are co-precipitated on the surfaces of the article by wetting the surfaces of the article with a succession of properly chosen solutions containing the component ions of the substances, the solution containing the anion of the sparingly water-soluble silver salt also containing a basic nitrogen compound, i.e., ammonia or an amine, which serves as a solubilizer for the sparingly soluble silver salt. After removal of the solubilizer by vaporization, or in any other convenient manner, the article containing the precipitated coating on its surfaces is washed with water to remove any remaining water-soluble compounds and is then dried. Under such conditions, it is found that the coating adheres tightly to the article and is very resistant to treatment with water, soap solution and the like and that such treatments reduce its bactericidal and fungicidal properties only very slightly, if at all.

It is advisable from economic considerations to use as low a proportion of the silver compound as possible to obtain the desired bactericidal effect. Generally speaking, from about 0.05 to about 1.0 per cent. by weight of silver compound in the coating will be found suitable, although somewhat lower proportions can often be used and higher proportions can, if desired, be employed.

The proportion of fungicidal compound can also be varied over a wide range, depending upon the fungicidal effectiveness of the particular compound employed, the particular organism which it is desired to control, and other factors. In most instances, when a salt of the preferred undecylenic acid is employed, the coating can with advantage contain from about 1.0 to about 10.0 per cent. by weight of the fungicidal compound, although lower proportions are often effective. Higher proportions can, of course, be used, if desired.

As has been indicated previously, the coating is useful for controlling fungicidal, bactericidal and virucidal infections and contaminations. The extent of its usefulness can be judged by its effectiveness *in vitro* in killing or preventing

the growth of such representative microorganisms as *Staphylococcus aureus*, *Escherichia coli*, *Colostridium welchii*, *Astridium sporogenes*, *Eberthella typhosus*, *Salmonella paratyphi*, *Proteus mirabilis*, *Shigella dysenteriae*, *Streptococcus hemolyticus*, *Diplococcus hemolyticus*, *Diplococcus pneumoniae*, *Aspergillus niger*, *Penicillium notatum*, *Trichophyton interdigitale*, *Trichophyton gypsum*, *Chaetomium globosum*, *Myrothecium verrucaria*, *Aspergillus terreus*, and the like.

In treating the article it may first be dipped in or wetted with an aqueous solution, herein referred to as a "first solution", containing a water-soluble silver salt, e.g., silver nitrate, and a water-soluble salt of a metal other than silver, e.g., magnesium nitrate, herein referred to as a "first salt", the cation of which is capable of forming a sparingly water-soluble salt with the anion of at least one other water-soluble salt, e.g., with a "third salt", to be referred to later. Excess of the first solution over that required to wet the article thoroughly is then usually removed mechanically, e.g., by squeezing, wringing, or wiping, after which the article usually while still wet, is dipped in or wetted with another aqueous solution, herein referred to as a "second solution", containing a water-soluble salt, e.g., sodium chloride, herein referred to as a "second salt", the anion of which is the anion of a sparingly water-soluble silver salt, a water-soluble salt, e.g., sodium phosphate, herein referred to as a "third salt", the anion of which is capable of forming a sparingly water-soluble salt with the cation of the first water-soluble salt, and ammonia or other water-soluble basic nitrogen compound as a "solubilizer" for the sparingly water-soluble silver salt. Excess of the second solution is then generally removed from the article, e.g., by squeezing, wringing or wiping, and the article is then dried thoroughly to vaporize the basic nitrogen compound, after which it can be washed to remove any excess of water-soluble salts and again dried. In some instances, the solubilizer is preferably neutralized or otherwise at least partially destroyed, e.g., in the case of ammonia or an amine, by adding a dilute acid, either prior to or after removal of the article from the second solution.

As a result of these operations there is precipitated on the surfaces of and in the interstices of the article a tightly adherent coating of a sparingly water-soluble silver salt comprising the anion of the second water-soluble salt, e.g., silver chloride, together with another sparingly water-soluble salt, e.g., magnesium phosphate, comprising the cation of the first water-soluble salt and the anion of the third water-soluble salt.

Articles treated according to the method described have been found to have an exceptionally high degree of self-sterilization which is retained substantially undiminished after dry cleaning or repeated laundering with hot

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soap solution. By a proper choice of the water-soluble salts, non-colored sparingly water-soluble salts are formed as a result of the treatment and it has been found that the non-colored sparingly water-soluble silver salts, e.g., silver chloride, deposited in this manner are remarkably resistant to darkening or discoloration upon exposure to strong light over long periods of time. Thus, it has been found that whereas a fabric treated according to the method just described can be exposed to light in an ordinary room for several weeks or months without the slightest tendency to darken, a sample of the same cloth subjected to treatment with the same identical first and second solutions, except for the omission of the first water-soluble salt from the first solution and of the third water-soluble salt from the second solution, begins to darken within a few hours and after a few days acquires the bluish-gray color characteristic of silver chloride which has been exposed to light for some time. Such coloration in the case of treated white goods cannot, of course, be tolerated. When colored fabrics are treated according to the method, a considerably greater latitude in the selection of salts to be included in the treating solutions can be exercised, since, in many instances, the formation of a colored salt on the article is not objectionable. Salts which are injurious to the article being treated should, of course, be avoided in both solutions.

In carrying out the preferred process, any convenient water-soluble silver salt can be used in the first solution. The nitrate is generally used because of its ready availability in a state of high purity. Other water-soluble or moderately water-soluble silver salts, such as silver lactate, silver acetate and silver fluoride, can, however, be used, if desired.

The first water-soluble salt should, of course be one which is compatible in solution with the water-soluble silver salt used to avoid the formation of a precipitate in the first solution. Salts of the alkaline earth metals are often preferred as the first salt because of the generally white nature of their salts and because they react with many relatively inexpensive soluble salts to form insoluble compounds. Water-soluble aluminum salts can often be used with advantage as will become apparent later. Water-soluble zinc salts appear to be of particular value in certain instances, particularly when a fungus-proofing treatment is desired. It also appears that the use of zinc salts is of particular value when exposure of the treated article to sulfur or sulfides may occur. Mixtures of "first" salts can, of course, be used if desired.

The second water-soluble salt, used in preparing the second solution, should, as mentioned previously, contain the anion of a sparingly water-soluble silver salt. For practical reasons, sodium chloride is generally used as the second salt because of its ready availability and low cost and because operation of the process to produce silver chloride as the sparingly water-soluble silver salt has been found to give excellent results. Other salts which can, however, be used as the second salt include potassium bromide, sodium iodide, sodium phosphate, calcium chloride, magnesium chloride and water-soluble halides of the heavy metals, as well as many others. It should be noted that the sparingly water-soluble silver salt which is formed need not be basic in character and, as a matter of fact, non-basic salts, such as the halides and phosphates, are generally preferred in the interest of economy and ease of operation of the process.

The third water-soluble salt, also used in preparing the second solution, should be compatible in aqueous solution with the second water-soluble salt to avoid the formation of a precipitate in the second solution. The choice of the third salt used will, of course, also depend in large measure upon the first salt used in the first solution since it is essential that the cation of the first salt and the anion of the third salt form a sparingly water-soluble compound as a result of the operation of the process. Salts which have been used successfully as the third salt when the first salt is a water-soluble calcium or strontium salt include the alkali metal and other water-soluble phosphates and sulfates. Sulfates are, of course, unsuited for use as the third salt when the first salt is a magnesium salt because of the solubility of magnesium sulfate in water. A water-soluble phosphate can, however, be used as the third salt in such instances. It is pointed out that it is impossible to give a precise list of salts, any one of which can be used in all cases as the first or second or third salt, because of the interrelationship of properties between these several salts which has been mentioned and which must be maintained by a proper selection of any one of the salts when specific salts have been selected as the other one or two salts.

The function of the solubilizer for the sparingly water-soluble silver salt appears to be related to the greater solubility of the sparingly water-soluble silver salt in the aqueous solution of the solubilizer than in water alone. In some instances, depending upon the particular first and third salts used in the process, the solubilizer may have a significant effect upon the character or solubility of the sparingly water-soluble silver salt formed in the operation of the process. Although ammonia is the preferred solubilizer, other basic nitrogen compounds which can be used include monoethyl amine, dimethyl amine, trimethyl amine, monobutyl amine, diisopropyl amine, monoethanol amine, diethanol amine, ethylene diamine, morpholine, pyridine, picoline and many others. Generally speaking, aliphatic amines, including the substituted alkylamines having

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less than about 10 carbon atoms in the molecule, are preferred to amines of higher molecular weight because of their greater volatility and ease of vaporization from the treated article during drying. Insofar as is known, however, any water-soluble basic nitrogen compound can be used in the process.

It is, of course, possible to choose the first, second and third salts so that the same compound can serve as the second and third salts, provided only that the anion of this compound forms a sparingly water-soluble salt both with silver as a cation and with the cation of the first salt. The process can thus frequently be carried out using magnesium nitrate as the first salt and sodium pyrophosphate alone in the second bath to serve as both the second and third salts. Generally, however, it is preferable to use a halide, preferably a chloride, as the second salt because of the favorable characteristics of the silver halides. It is also possible in some instances, i.e. when the first salt is an aluminium salt, for ammonium hydroxide to serve as the third salt, the compound deposited with silver salt in this instance being aluminium hydroxide.

The proportions of the several salts used in making up the solutions both with respect to the solvent and with respect to one another can be varied over wide ranges. In the interest of economy, however, the water-soluble silver salt and the second salt are used at concentrations in the first and second solutions, respectively, such that the amounts of the solutions used in wetting the article being treated will contain the second salt in at least a stoichiometric ratio to the water-soluble silver salt, and preferably somewhat more. The same applies, in general, to the proportions of the first and third water-soluble salts. It is apparent that an influential factor is the character of the article being treated, including its absorptive capacity and surface characteristics, and that it is substantially impossible to define the first and second solutions in terms of the concentration of the salts therein. It has been found that good results are obtained when the amount of sparingly water-soluble silver salt deposited in or on a fibrous fabric is from about 0.1 to about 0.5 per cent, calculated as silver chloride, of the weight of the fabric, together with from about 0.05 to 1.0 per cent of the weight of the fabric of the other sparingly water-soluble salt deposited with it. Here again, however, it is not possible to define these values quantitatively with any degree of satisfaction because of the number of variables involved in passing from one instance to another.

Certain other ingredients may often be included in the treating solutions with advantage. In some instances a wetting agent can be included to promote wetting and penetration of the article being treated. In some instances, also, the inclusion of a dispersed resin, e.g., an

emulsified polyvinyl acetate, in one or the other of the solutions, usually the second, leads to a more permanently self-sterilizing product. This may be due to the resin acting in the nature of a binder for the co-precipitated salts.

In the production of articles having highly fungicidal as well as germicidal properties, the article may first be treated with a solution of a water-soluble calcium salt, such as calcium chloride, and then with a solution of the ammonium, sodium or other water-soluble salt of undecylenic acid, or vice versa, these treatments being carried out either prior to or subsequent to the treatment with the first and second solutions previously referred to. Somewhat better results appear to be obtained when the treatment with the first and second solutions is carried out subsequent to the treatments with the calcium salt and undecylenic acid salt solutions. One preferred procedure comprises incorporating a water-soluble calcium salt, such as calcium nitrate, in the first solution along with the water-soluble silver salt and incorporating the water-soluble undecylenate, e.g., ammonium undecylenate, in the second solution along with the second and third water-soluble salts. Under such conditions a desirable co-precipitation of the calcium undecylenate along with the sparingly water-soluble silver salt is realized.

Considerable latitude is possible in the selection of the sparingly water-soluble silver salt which can be employed, due consideration being given to the facts that it must furnish a germicidal concentration of silver ions in contact with water or adsorbed moisture but that it must not be sufficiently soluble to be removed easily by washing or to lead to the undesirable effects in the way of discoloration generally encountered when attempting to use a highly water-soluble silver salt, such as the nitrate, as a germicide. The sparingly water-soluble silver salts which can be used have a solubility in water greater than about that of silver sulfide but not appreciably greater than about that of silver sulfate. For most practical purposes, the silver compound selected will be a halide or a phosphate. In most instances silver chloride is preferred because of its advantageous solubility characteristics and because of its ready availability whether used as such or whether prepared during the operation of the process by precipitation methods. It has also been observed that the halides of silver, particularly the chloride, are somewhat less liable in the presence of the light stabilizer to become discoloured upon exposure to sunlight than are the phosphates and that when using the phosphate a higher ratio of light stabilizing compound to silver compound is generally desirable than when using silver chloride.

The light stabilizers referred to herein are, in many instances, inorganic compounds which are highly insoluble in water and which, when

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in aqueous admixture with the silver compounds, do not deplete the silver ions in the mixture to an extent such that the mixture is no longer germicidal. For most applications where a non-colored product is involved, the light stabilizer should, of course, be non-colored. Examples of specific light stabilizer compounds which can be used include water-insoluble phosphates, sulfates, silicates, and many other simple and complex inorganic salts. Generally speaking, the phosphates of the alkaline earth metals, including magnesium, are preferable from a practical standpoint because of their ready availability, low cost and advantageous solubility and color characteristics. Such substances as alumina, silica, calcium carbonate, zinc oxide and magnesia can also be employed advantageously. It should be mentioned that where certain shades of color are not an objection it is possible to carry out the process in such a way as to employ a colored silver salt and a colored light stabilizer provided the color of such compounds is substantially the same as that of the composition or article desired. Articles of certain shades of yellow can, for example, be prepared utilizing a chromate as the anion of both the silver salt and the light stabilizer.

The preferred fungicidal organic acids are the saturated and unsaturated organic acids having from 3 to 11 carbon atoms in molecule. Such acids include propionic, caproic, caprylic, pelargonic, undecylenic, valeric, sorbic, oleic, and hexenoic acids. In addition to these, however, fungicidal organic acids of other series can be employed, such as benzoic and salicylic acids. Salts of the fungicidal acids which are of particular value are the sparingly soluble aluminum, zinc, magnesium and alkaline earth metal salts. Here again, a colorless salt is preferred although colored salts can be used in certain instances as referred to above. The fungicidal salt should, of course, be chosen with due regard to its toxicity to the higher animals where this is a factor. The fungicidal salt should also furnish, when the composition is in contact with water, a fungicidal concentration of the organic acid anions but should not deplete the aqueous mixture of silver cations to such an extent that the germicidal effectiveness of the latter is impaired. It has been found in practice that the alkaline earth metal salts of undecylenic acid, particularly calcium undecylenate which has not been described previously, can generally be used with advantage. In certain instances, silver undecylenate can be employed as both the germicidal and the fungicidal agent.

In the examples which are given below, the products prepared were tested in most instances using a modification of the United States Food & Drug Administration method for assaying penicillin employing an agar medium. The article was said to be self-sterilizing when no significant cloudiness developed in

the medium around the sample. In certain other instances, the treated sample was shaken for several hours in a closed container with sterile distilled water which had been inoculated with a suspension of the organism employed in the particular test. The microbicidal properties of the treated sample were judged by its effect on the cell population in the inoculated water.

EXAMPLE 1.

A first solution was prepared by dissolving 10 grams of silver nitrate and 20 grams of hydrated magnesium nitrate in 1000 milliliters of distilled water. A second solution was prepared by dissolving 6 grams of sodium chloride, 30 grams of disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and 200 milliliters of aqua ammonia in 800 milliliters of distilled water. A sample of white cotton sheeting was immersed for a period of 30 to 60 seconds in the first solution and then removed and squeezed tightly to eliminate excess solution. The squeezed cotton sheeting contained about 150 per cent., based on its dry weight, of solution. The still wet cotton sheeting was then immersed in the second solution for 30 to 60 seconds and then removed, squeezed and dried thoroughly. The dried cotton sheeting was then washed in clear water to remove excess soluble salts and again dried. The product prepared in this manner was found to be both antiseptic and self-sterilizing. It had a hand and feel substantially identical with that of untreated cotton sheeting which had been washed in clear water and dried. The color of the treated fabric was indistinguishable from that of washed untreated fabric. Samples of the treated cotton sheeting exposed to strong sunlight daily for as long as 60 days showed no tendency to become discolored.

A number of samples of the treated cotton sheeting were washed repeatedly in a home washer using a good grade of soap and with the washing bath at about 90° C. The samples were rinsed and dried after each washing. After each period of several washings, one or more of the samples was removed and tested for antiseptic and self-sterilizing properties. After as much as 100 washing and drying cycles, the samples still had significant and adequate antiseptic and self-sterilizing properties.

The experiment was duplicated with the cotton sheeting being replaced with cotton gauze, woolen uniform cloth, woolen cloth for civilian use, blended wool and cotton cloth, woolen blankets containing both virgin wool and reprocessed wool, acetate rayon fabrics, surgical masks, surgeon's hats, filter paper, cotton diapers, and woolen, cotton and acetate rayon socks and underwear. In each case the treated product was antiseptic and self-sterilizing, was substantially unchanged in its hand and feel and was not discolored by prolonged exposure to light. In the case of heavy fabrics,

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such as wool blankets, the samples were soaked in each of the separate solutions for about two minutes. A number of the treated fabrics mentioned were laundered and dry cleaned repeatedly without lowering their antiseptic and self-sterilizing properties appreciably.

Variations of the process were carried out by drying the final washed product in an oven at 60°—70° C., by drying the article after wetting with the first solution and before wetting with the second solution, and by carrying out the dipping steps with the first solution heated at 60°—80° C. None of these variations in the process produced any significant change in the treated article. It was noted that at higher dipping temperatures, e.g., at about 80°—100° C., a small amount of a dark pre-

cipitate gradually formed in the first solution upon prolonged exposure to light.

In still other variations of the experiment, the squeezing of the sample after wetting with the first solution was varied so as to leave as little as 100 per cent. or as much as 200 per cent. of the first solution, based on the dry weight of the sample, absorbed on the sample. No significant differences in the results were noted.

EXAMPLE 2.

The procedure described in Example 1 was repeated using a variety of first and second treating solutions, the compositions of which are given below in tabular form as Treatments "A" to "Q" inclusive:—

TABLE OF TREATMENTS.

	Treatment	First solution	Second solution
35	A	5g. AgNO ₃ 5g. Mg(NO ₃) ₂ :6H ₂ O 1000 ml. H ₂ O	3 g. NaCl 5 g. Na ₂ PO ₄ :12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
40	B	5g. AgNO ₃ 5g. Mg(NO ₃) ₂ :6H ₂ O 1000 ml. H ₂ O	3 g. NaCl 5 g. Na ₂ PO ₄ :12H ₂ O 200 ml. NH ₃ (Aq) 10 g. resin emulsion 800 ml. H ₂ O
45	C	10 g. AgNO ₃ 1 g. Mg(NO ₃) ₂ :6H ₂ O 1000 ml. H ₂ O	5 g. NaCl 15 g. Na ₂ PO ₄ :12H ₂ O 150 ml. NH ₃ (Aq) 850 ml. H ₂ O
50	D	8 g. AgNO ₃ 8 g. Mg(NO ₃) ₂ :6H ₂ O 1000 ml. H ₂ O	5 g. KCl 8 g. K ₂ P ₂ O ₇ :3H ₂ O 125 ml. NH ₃ (Aq) 875 ml. H ₂ O
55	E	10 g. AgNO ₃ 8 g. Ca(NO ₃) ₂ :3H ₂ O 1000 ml. H ₂ O	6 g. NaCl 8 g. K ₂ P ₂ O ₇ :3H ₂ O 150 ml. NH ₃ (Aq) 850 ml. H ₂ O
60	F	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1000 ml. H ₂ O	7 g. NaCl 10 g. Na ₂ SO ₄ 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
65	G	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1000 ml. H ₂ O	7 g. NaCl 10 g. Na ₂ SO ₄ 14 g. resin emulsion 180 ml. NH ₃ (Aq) 820 ml. H ₂ O
70	H	10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1000 ml. H ₂ O	6 g. NaCl 10 g. Na ₂ SO ₄ 15 g. resin emulsion 100 ml. monoethanol amine 100 ml. NH ₃ (Aq) 800 ml. H ₂ O

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TABLE OF TREATMENTS, (cont.)		
Treatment	First solution	Second solution
5	I 10 g. AgNO ₃ 15 g. Ba(NO ₃) ₂ 1000 ml. H ₂ O	7 g. NaCl 10 g. Na ₂ SO ₄ 160 ml. monoethanol amine 840 ml. H ₂ O
	J 10 g. AgNO ₃ 10 g. Al(NO ₃) ₃ :9H ₂ O 1000 ml. H ₂ O	5 g. NaCl 200 ml. monoethanol amine 800 ml. H ₂ O
10	K 10 g. AgNO ₃ 10 g. Al(NO ₃) ₃ :9H ₂ O 1000 ml. H ₂ O	5 g. NaCl 100 ml. monoethanol amine 150 ml. NH ₃ (Aq) 750 ml. H ₂ O
15	L 10 g. AgNO ₃ 5 g. Al(NO ₃) ₃ :9H ₂ O 5 g. Mg(NO ₃) ₂ :6H ₂ O 1000 ml. H ₂ O	5 g. NaCl 5 g. Na ₃ PO ₄ :12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
20	M 10 g. AgClO ₄ 10 g. Al(NO ₃) ₃ :9H ₂ O 1000 ml. H ₂ O	5 g. NaCl 280 ml. NH ₃ (Aq) 720 ml. H ₂ O
	N 10 g. AgNO ₃ 10 g. Al(NO ₃) ₃ :9H ₂ O 1000 ml. H ₂ O	10 g. NaBr 300 ml. NH ₃ (Aq) 700 ml. H ₂ O
25	O 10 g. Mg(NO ₃) ₂ :6H ₂ O 1000 ml. H ₂ O	10 g. Na ₃ PO ₄ :12H ₂ O 3 g. AgCl 250 ml. NH ₃ (Aq) 750 ml. H ₂ O
30	P 10 g. AgClO ₄ 10 g. Al(ClO ₃) ₃ :6H ₂ O 1000 ml. H ₂ O	5 g. NaCl 280 ml. NH ₃ (Aq) 720 ml. H ₂ O
	Q 10 g. AgNO ₃ 10 g. Ca(NO ₃) ₂ :3H ₂ O 1000 ml. H ₂ O	6 g. NaCl 10 g. Na ₂ SiO ₃ 150 ml. NH ₃ (Aq) 850 ml. H ₂ O

35 In every instance, except as noted, the treated fabric was antiseptic and self-sterilizing and resistant to discoloration upon exposure to light. The fabric treated using Treatment "N" was initially yellowish in color due to the presence of yellow silver bromide on it but it was antiseptic and self-sterilizing. It is noted that in Treatment "O" the water-soluble silver salt in the first solution was replaced with silver chloride dissolved in the ammoniacal second solution. Cotton cloth treated according to Treatment "O" was not stable against discoloration by light. Furthermore, when the ammonia in Treatment "O" was replaced with an equivalent quantity of mono-

ethanol amine, the treated sample discolored 50 completely when exposed to sunlight for three days. No such discoloration occurred in the case of Treatments "H", "I", "J" and "K". The antiseptic and self-sterilizing qualities of the treated fabric were, however, satisfactory using either ammonia or monoethanol amine in Treatment "O". 55

EXAMPLE 3.

Cotton sheeting was treated by the procedure described in Example 1 using first and 60 second treating solutions, the compositions of which are given below in tabular form as Treatments "R" to "U", inclusive.

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TABLE OF TREATMENTS.

	Treatment	First solution	Second solution
5	R	10 g. AgNO ₃ 15 g. Zn(NO ₃) ₂ ·6H ₂ O 1000 ml. H ₂ O	6g NaCl 27 g. Na ₃ P ₂ O ₇ ·10H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
10	S	10 g. AgNO ₃ 15 g. Zn(NO ₃) ₂ ·6H ₂ O 1000 ml. H ₂ O	6 g. NaCl 24 g. Na ₃ PO ₄ ·12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
	T	10 g. AgNO ₃ 13 g. Al(NO ₃) ₃ ·9H ₂ O 15 g. Zn(NO ₃) ₂ ·6H ₂ O 1000 ml. H ₂ O	8 g. NaCl 25 g. Na ₃ PO ₄ ·12H ₂ O 200 ml. NH ₃ (Aq) 800 ml. H ₂ O
15	U	10 g. AgNO ₃ 13 g. Al(NO ₃) ₃ ·9H ₂ O 15 g. Zn(NO ₃) ₂ ·6H ₂ O 1000 ml. H ₂ O	32 g. CaCl ₂ 200 ml. NH ₃ (Aq) 800 ml. H ₂ O

Nutrient agar was prepared, some of which contained 0.01 per cent. of sodium thioglycolate and some of which contained 0.02 per cent. cystine. Samples of sheeting which had been subjected to Treatments "R", "S", "T" and "U" were tested using each of these nutrients according to the method of Example 1. In each instance the test showed the treated sheeting to be both antiseptic and self-sterilizing even in the presence of the cystine and sodium thioglycolate. No discoloration of any of the treated samples occurred on contact with the agar.

Further tests of the sheeting which had been subjected to Treatments "R", "S", "T" and "U" were made using Sabourauds dextrose agar (10 g. peptone, 40 g. dextrose, 15 g. agar and 1000 ml. distilled water) at pH 5.6 and employing *Trichophyton gypsum* and *Aspergillus itaconicus* (Glaucus group) as the test organisms. Incubation was for seven days at room temperature. No growth of either organism occurred on the treated samples.

EXAMPLE 4.

A sample of foam rubber was boiled with sodium thiosulfate to remove free sulfur and washed thoroughly with water. It was then boiled with an aqueous solution of copper sulfate to neutralize accelerators, such as sodium dibutyl-diethiocarbamate, and was treated and tested according to the method of Example 1. The sample was self-sterilizing and antiseptic.

EXAMPLE 5.

Four solutions were prepared having the compositions given under "d", "e", "f" and "g" below.

Solution "d"
10 g. undecylenic acid
20 ml. ammonia (Aq)
1000 ml. H₂O

Solution "e"
10 g. CaCl₂
1000 ml. H₂O 60

Solution "f"
10 g. AgNO₃
5 g. Mg(NO₃)₂·6H₂O
1000 ml. H₂O 65

Solution "g"
8 g. NaCl
10 g. Na₃PO₄·12H₂O
16 g. resin emulsion
150 ml. ammonia (Aq)
850 ml. H₂O 70

Men's cotton socks were dipped successively in one case in solutions "d", "e", "f" and "g" and in another case in solutions "e", "d", "f" and "g", the socks being wrung fairly dry after each dip. The socks were finally dried and then washed thoroughly with water and again dried. Samples cut from the treated socks were tested by placing them on agar inoculated with *Trichophyton gypsum*. After incubation for 7 days at room temperature, no growth of the organism on the sample was apparent. Identical results were obtained on samples of the treated socks after ten launderings in hot soap solution. 85

What I claim is:—

1. An article having on the surfaces thereof a coating comprising a co-precipitated mixture of a sparingly water-soluble silver salt and at least one other sparingly water-soluble compound of another metal of such a nature that it functions as an effective stabilizer of the silver salt against the effect of light normally tending to discolor the silver salt. 90

2. An article as claimed in Claim 1, wherein the silver salt is a silver halide or a silver phosphate. 95

3. An article as claimed in Claim 1 or 2, wherein the silver salt is a silver chloride.

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4. An article as claimed in any of the preceding claims, wherein the anions of the silver salt and of the compound of the other metal are the same.
5. An article as claimed in any of the preceding Claims 1 to 4, wherein the anions of the silver salt and of the compound of the other metal are different.
6. An article as claimed in any of the preceding claims and which is fibrous in nature.
7. An article as claimed in any of the preceding claims, wherein a sparingly water-soluble fungicidal compound of a fungicidal organic acid is intimately co-mingled with the silver salt.
8. An article as claimed in Claim 7, wherein the fungicidal compound is a salt of an aliphatic acid having from 3 to 11 carbon atoms.
9. An article as claimed in Claim 8, wherein the metal used in forming the salt is an alkaline earth metal, or magnesium, zinc or aluminium.
10. An article as claimed in any of Claims 7 to 9, wherein the fungicidal compound is a salt of undecylenic acid.
11. An article as claimed in any of Claims 7 to 10, wherein the fungicidal compound is calcium undecylenate.
12. The method for treating an article to render it microbicidal, which includes the steps of contacting the article with a first aqueous solution comprising a water-soluble silver salt and a first water-soluble salt of another metal, the cation of which is capable of forming a sparingly water-soluble salt with an anion of at least one other water-soluble salt, subsequently contacting the thus treated article with a second aqueous solution containing a second water-soluble salt, the anion of which is the anion of a sparingly water-soluble silver salt, and a third water-soluble salt, the anion of which forms a sparingly water-soluble compound with the cation of the first water-soluble salt, and a water-soluble basic nitrogen compound, whereby a sparingly water-soluble silver salt and a sparingly water-soluble metal compound are formed, the metal compound functioning as a light stabilizer of the silver salt against the effect of light normally tending to discolor the silver salt.
13. The method as claimed in Claim 12, wherein the basic nitrogen compound is ammonia or an amine.
14. The method as claimed in Claim 12 or 13, wherein the second and third water-soluble salt are the same salt.
15. The method as claimed in Claim 12 or 13, wherein the water-soluble silver salt is silver nitrate, the first water-soluble salt is magnesium nitrate and the third water-soluble salt is sodium phosphate.
16. The method as claimed in Claim 12, wherein the first aqueous solution includes a water-soluble salt furnishing cations for a sparingly water-soluble salt of which the anions are fungicidal and the second solution includes a water-soluble salt whose anions are the said fungicidal anions.
17. The method of treating an article to render it microbicidal, substantially as hereinbefore described with reference to any of the specific examples.
18. Coated articles whenever prepared or produced by the method claimed in any of Claims 12 to 17.

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